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From the editors

Welcome to the latest issue of the Caltech Undergraduate Research Journal (CURJ)! As we turn another page into a New Year, let us take a quick look at Caltech’s accomplishments. The year 2012 witnessed a second consecutive year of Caltech’s dominance atop Times Higher Education’s World University Rankings. Despite its small size, Caltech has been producing some of the best innovations year after year. Everything from beginning another era in Mars exploration with the landing of Curiosity to revolutionary advances in solar-powered toilet technology truly embodies the Caltech motto of “the truth shall make you free.”

This ongoing creativity and progress is no doubt largely due to the collaboration and hard work of individuals at all educational levels, spanning across a multitude of fields. Yet what sets Caltech apart from any other research institution is its unique nurturing atmosphere. Not only do Caltech students have ample opportunities to gain valuable research experiences that train them to think rigorously like real scientists, but the encouragement from the administration and faculty for undergraduate research is also unrivaled by any other institution.

CURJ is honored to partner with Caltech’s Summer Undergraduate Research Fellowship program to highlight some of the cutting edge research done at Caltech by four young scientists: Phillip Daniel, Claire Drolen, Jingyuan Li, and Elizabeth Ryan. Their research topics range from screening for photocatalysts for the reduction of carbon dioxide as an energy source to fabrication of multi-surface adhesion materials. With all the exciting student research at Caltech, let us not forget the overwhelming support of dedicated faculty and mentors. CURJ would like to take this opportunity to thank all the faculty and mentors for their dedication and investment in future scientists. Moreover, CURJ is proud to feature interviews of Professors John Grotzinger and Erik Snowberg in this issue.

Professor Grotzinger is a renowned expert on the chemical development of early oceans and atmosphere and its effect on animal evolution. Furthermore, Professor Grotzinger also serves as the chief project scientist on NASA’s Curiosity rover in its mission to discover Mars’ potential to support microbial life. On the other hand, Professor Snowberg specializes in the relationship between economics and politics and leads his field by using models to predict political and economic change. Caltech is surely privileged to have figures like these two individuals, each leading the way in their respective fields.

Lastly, we thank you for picking up this latest edition of CURJ and certainly hope that you enjoy it. You can find more CURJ information as well as previous issues on our website (curj.caltech.edu). As always, feel free to let us know your thoughts.

Best regards,

Marvin Gee and Conway Xu
Interview with Professor Erik Snowberg

By Conway Xu

Erik Snowberg is a Professor of Economics and Political Science in the Division of Humanities and Social Sciences at Caltech. Professor Snowberg received his S.B. in Physics and Mathematics as well as a minor in Economics from MIT. After graduation, he shifted focus and went on to receive a Ph.D. in Business Administration from Stanford. His research interests currently include combining political and behavioral economics as well as using economic theories to design better randomized controlled trials for development economics, public health, and medicine.
As someone who has an extensive undergraduate training in the fields of physics and mathematics, what initially sparked your interest and what made you eventually interested in getting into political science?

I really got into physics in high school. In AP Physics, we would perform experiments like rolling a ball down the ramp, and trying to get it into a coffee can. When it landed in the can you’d get this “Oh cool – I did something” feeling.

This initial “spark” followed me to MIT, but by the time I got to Quantum Physics 3, I realized that physics had drifted too far from the ball-in-a-coffee-can experiments. Everything had turned from concrete concepts to abstracts ideas like bra-ket notation and wave functions. At that point, it was a year before graduation and a little too late to change majors, so I really did not know what I was going to do after college.

Luckily, MIT had a DC internship program where students could get exposed to policy side of science. The program allowed me to intern with the House Committee on Science after my junior year, which was a great experience. Up until that point, I had never had any interest in politics, but I thought that if even I could get interested, so could anyone else. After the summer, I tried to get my classmates interested in politics as well. This eventually led to the idea of getting a student to run for the city council in the hopes of exciting the student population to vote. However, no one else wanted to run, so I ended up being that student. Despite defeat in the election, the whole experience gave me some notoriety and connections that would later prove valuable. After graduation, I worked for a bit before moving back to Boston and getting in touch with some of my professors at MIT. While working fulltime, I did some political science research with them and eventually went to graduate school on their recommendation.

What do you study now at Caltech? How did you get into this kind of research?

My major research involves two overarching ideas. One is using economic theory to inform the design of randomized control trials in various fields including medicine and public health. The other half is trying to connect behavioral economics and political science. This involves using theories and ideas in behavioral economics to build models that predict people’s political behavior. I initially wrote about these ideas in my graduate school application essay, but there was never really anyone around to focus on these ideas in graduate school, so they had to wait until I got to Caltech and had interested colleagues.

Have you had any SURF students, and what were their projects?

I have had a few SURF students. My first summer as an Assistant Professor I had a SURF student work on was how religious figures talked about politics. This involved collecting a large database of sermons and conducting textual analysis on them. I was really impressed by that student’s skills and determination to work through a difficult set of challenges.

During a time of shrinking federal budgets, there is simply not going to be a lot of people who are going to get angry over cutting funding from basic research and development.”
Switching gears now, can you tell us a little about scientific policy in recent years and what changes you anticipate after President Obama’s reelection?

The last people who made significant contributions to expanding funding for science were President Clinton and Speaker Gingrich. Since then, Congress has not paid much attention to science, and basic research and development. This is a real problem because our economic models show that basic research and development is underprovided relative to what would be socially efficient. In recent years science funding has not been cut, instead, it has not kept pace with inflation and population growth.

In all, I do not think that science has really received a lot of attention from anyone under the Bush or Obama administrations. During a time of shrinking federal budgets, there is simply not going to be a lot of people who are going to get angry over cutting funding from basic research and development. As such, I do not foresee big changes in science policy with the current trend of the economy.

Without increases in funding, the agencies that fund basic research have developed their own problems. They seem to only want to fund “sure things”, projects that will definitely produce returns, rather than more exploratory work.

“The biggest challenge has been overcoming self-doubt and worry about whether or not I would “make it”. That is still a challenge to this day.”

Why do you think it’s important to study political science?

That’s a tough question. For the economy to function, there are many prerequisites such as property rights and the right to free exchange. However, markets do not maintain these conditions on their own accord, which is precisely why political systems are needed. That is, political systems are responsible for creating the institutions that allow for economic prosperity and growth.

Furthermore, we now know a decent bit about how markets function, but we still know relatively little about how political systems function. Macroeconomics has realized the importance of good institutions, but our attempts to create good institutions often end in failure, and tend to make things work. There is a big difference between understanding the importance of something, and knowing how to make it happen.

What is the biggest challenge along your career path thus far? What advice do you have for those students interested in political science?

The biggest challenge has been overcoming self-doubt and worry about whether or not I would “make it”. That is still a challenge to this day.

I once asked my physics advisor what classes I should take to become a better physicist. He told me that he thought I should take a ballet class. When I asked why, he told me “You like ballet, don’t you?” When I told him I didn’t he said, “Well, then you probably shouldn’t take a ballet class then.” What he meant was that if you take classes you enjoy, then you’re more likely to be good at them, and everything else in your life. Don’t try to be good at something, try to do what you enjoy, and maybe you’ll be good at it. And if not, at least you had fun.
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Interview with Professor John Grotzinger

By Nikita Sinha

Professor John P. Grotzinger received his Ph.D. from Virginia Polytechnic Institute and State University in 1985 and became a professor at MIT in 1987. He is now the Fletcher Jones Professor Geology at Caltech under the Division of Geological and Planetary Sciences. His research interests include sedimentology, stratigraphy, geobiology, and ancient surface processes on Earth and Mars. He is currently the Project Scientist for the NASA Mars Science Laboratory rover mission.

You have become a well-established professor at a great institution. What was your path here including your interests in undergraduate and graduate school? What was your motivation?

I was always interested in the sciences. Late in my career as an undergraduate, I discovered geology and realized that you could combine all the sciences, plus do it outdoors. I was particularly interested in collection of data based on field work, and then being able to analyze it back in the lab.

Did your undergraduate experiences define your ultimate career path? If so, why? What was your most memorable academic experience in undergraduate and graduate school?

I vividly recall my first field trip where we were able to discover that the rocks preserved evidence for an ancient ocean that had once been present in upstate New York. We reached that conclusion by observing casts of soluble salt minerals - long since vanished - that betrayed the former presence of salt water in rocks hundreds of millions of years old. It was recognizing that chemistry could be applied to understanding the state of the very ancient Earth that really got me interested in changing my major. In graduate school I recall my first field trip that started in Calgary and ended in Vancouver - a transect of the Rocky Mountains - and learning how plate tectonics shapes the Earth. It was a great trip because all of grad students bonded together and also learned a ton of geology, all while doing it outdoors.

What has been a major challenge you have faced along your journey?

Making geological maps is like solving jig saw puzzles. Geologic maps form the basis for reconstruction of all chronologic events in the history of the Earth, so it is important to get it right. But you only get really good at it by doing more and more of it. So sooner or later you’re going to be spending a lot of time away from your friends and family, and working in far flung places. This can be really hard at times.
CURJ’s goal is to publish significant undergraduate research. What are some of your views on undergraduate research experiences, and how does it shape future scientists?

I am a big believer in undergraduate research. It was not until I started my own undergraduate research project that I finally realized I wanted to do research for my career. No amount of book-learning can substitute for this experience. The process of formulating a good question - one that can be addressed in a limited amount of time - and the development of a plan to address that question, and then to execute the plan, is really special. We often think that getting good data that helps test a hypothesis is the key reward in doing research, but I have always found the most pleasure in finding a good question. When you finally think of a good one it just feels right.

“Do what you love, love what you do, and don’t promise more than you can deliver.”
What has your experience been with undergraduate students? Have you had any SURF students or undergraduate researchers work in your lab?

I’ve had a couple of students over the years. It’s always great to see them catch on to the research question themselves, and then become independent and build confidence as they execute their research plan.

The advances you’ve made are quite incredible. Could you explain what your research is about and the significance of its impact?

What we’re doing with Curiosity is exploring the early environmental evolution of Mars. This is really a remarkable time in the history of Mars because we have many reasons to believe it was more like Earth then, with abundant aqueous environments. In fact, the rocks were working on with Curiosity are likely older than the oldest well-preserved rocks on Earth that preserve environmental records. So if Mars and Earth were similar early in their histories, then maybe studying Mars can help us fill in some gaps in our understanding of early Earth. But mostly we study early Mars to learn about early Mars, and we learn something new every day.

How has being the chief scientist on the Curiosity project been?

Working on the Curiosity mission is very different for me. I’m used to being by myself, or with just a few students and colleagues, out in the field somewhere. Now I’m responsible for the execution of a research plan being conducted by hundreds of scientists. There is the excitement of learning an amazing number of new things basically every day. You can’t lose - someone always has something new to share or show you.

What is Curiosity up to now? What are some Mars mysteries that Curiosity might help solve in the future?

Our biggest question is whether or not early Mars had environments that could have supported microbial life, if life had ever originated there. Right now we’re looking at some pretty geology that we’ll be able to study by drilling a hole, collecting the power, and analyzing it with our onboard analytical instruments. We hope to begin drilling by mid-January.

From personal experience, what advice do you have for Caltech undergraduate students?

Do what you love, love what you do, and don’t promise more than you can deliver.

“There is the excitement of learning an amazing number of new things basically every day. You can’t lose - someone always has something new to share or show you.”
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End Effector Design and Fabrication for Multi-Surface Adhesion
"A successful gripper design must be insensitive to surface orientation and geometry, and be capable of functioning in a microgravity environment."

INTRODUCTION

Robotic gripping in outer space is of interest to engineers because it would allow a payload to be securely attached to space debris. This would allow for new interactions with the debris including part salvage, repair, and disposal. Moreover, adhesive gripping would enable robots to carry out inspection and repair tasks on the International Space Station which currently can only be performed by human astronauts. Yet all of these applications require an adhesion technique that can function in outer space, as the low Earth orbit environment renders most conventional gripping methods ineffective or impractical. Tacky adhesives are quickly soiled during operation in such an environment and are unable to readily release from a surface without high pull-off forces, which reduce their adhesive capabilities. Suction depends on the dense atmosphere around a relative vacuum, which cannot be found in the low Earth orbit. Finally, a grasping method akin to the fingers of the human hand requires high precision sensors and restricts interaction to a limited number of gripping points on an object. Instead, a single adhesive method is needed that allows for controllable On-Off adhesion and requires low engagement pre-load and detachment forces. This solution must also, most importantly, function in outer space.
One possible solution, which satisfies the critical constraints, is a gecko inspired adhesive skin. Geckos can repeatedly adhere to the surface of materials with various roughnesses and geometries. Additionally, the adhesive strength of a gecko’s skin is controlled by the amount of shear pressure it undergoes. This allows the engagement and detachment forces to be negligible, as the skin is no longer sticky once the applied shear force is reduced to zero or reversed. Because of these natural properties, a synthetic skin was developed that greatly mimics the skin of a gecko.

This synthetic skin is a dry adhesive, meaning that it does not feel tacky to the touch, and functions by taking advantage of van der Waals forces. In any adhesive material that utilizes van der Waals interactions, the bond strength is proportional to the real area of contact between the adhesive surface and the bonding surface. As a result of surface asperities, the real area of contact is usually less than the projected area shared by two overlapping surfaces (Figure 1).

In order to achieve the intimate real area of contact needed for the van der Waals forces to be significant, geckos use a hierarchical microstructure. This microstructure conforms to surface asperities from the centimeter scale to the nanometer scale to increase the contact between the gecko’s skin and a surface (Figure 2). Due to the physical orientations of these features, the adhesion is unidirectional.

In order to imitate the unidirectional nature of a gecko’s skin, the synthetic material was developed with unidirectional features at the setae scale. This skin was then attached to a suspension layer, which added conformation at the millimeter scale by imitating the gecko’s lamella. Manufacturing limitations prevent the replication of the setae’s geometry or the creation of structures at the spatula scale. However, the synthetic material is still able to adhere to a surface through the same process as the biological skin (Figure 3). Each color/shape represents an adhesive with a different hierarchy version. Hier III was used for the project because it has the greatest adhesive range. Since the magnitude of the shear pressure is significantly greater than the magnitude of the normal pressure, the majority of previous work on this adhesive took advantage of its shear properties, culminating in the design of vertical climbing robots. Yet this work is less useful for gripping objects in outer space, as it assumes that the load will be predominantly shear and due to the acceleration of gravity. New work was done to explore omnidirectional, compliant gripping.

**FIGURE 1**
The real area of contact between two materials that are touching. Upon contact, both materials deform so that the peaks of some of the surface asperities are touching. The real area of contact (shown in blue) is the area between the deformed asperities, which is less than the area shared by the two surfaces. (Prof. Dr. H.-J. Güntherodt, 2002)
FIGURE 2
The hierarchical microstructure of the gecko foot at its different levels of conformation, from the toe at the centimeter scale, the lamellae at the millimeter scale, the setae at the micrometer scale, and the spatula at the nanometer scale. (Top: Elliot Hawkes, 2011; Bottom: Kellar Autumn, 2006)

FIGURE 3
The micron-scale structures are triangles that are slightly biased towards one direction. This bias is what gives the organic and synthetic adhesives their unidirectionality. When a shear load is applied to the material, the stalks bend to lie against a surface, increasing the real area of contact and allowing adhesion. Because of the directional bias, the stalks only bend effectively in one direction, as is true with the gecko’s skin. (Elliot Hawkes, 2011)
OMNIDIRECTIONAL GRIPPER DESIGN

A successful gripper design must be insensitive to surface orientation and geometry, and be capable of functioning in a microgravity environment. In order to achieve this, the end effector of the proposed design was built to operate in the same way that a gecko does when it reorients its feet to climb non-vertically. There are two main components to the current gripper design which contribute to its omnidirectional functionality: the body, which determines the pattern of the adhesive, and the ankle, which allows the gripper to conform to curved and rough surfaces.

THE BODY

The body was designed to allow the adhesive pads to pull towards the center of the gripper, like the feet of a climbing gecko (Figure 5). This arrangement of the pads allows the mechanism to support and adhere to a load in any direction.

THE ANKLE

Another key to the functionality of the design is the ankle, which allows the mechanism to adhere to curved surfaces. The ankle design was based on the ankle mechanism used by Stanford’s Biomimetics Robotics Lab for vertical climbing (Figure 6).

FIGURE 5
An image of the omnidirectional gripper. The body arranges the adhesive radially, like the feet of a gecko when it is climbing non-vertically.

FIGURE 6
A representation of the ankle that was developed at Stanford University for vertical climbing. The tile is loaded through the back plate/forelimb extension. This allows a free-string, which is attached to the back plate, to be pulled at an angle larger than the tendon angle that the adhesive can support on its own. The pulley keeps the string nearly parallel to the adhering surface, so the adhesive is always predominantly sheered. This allows the adhesive to be less sensitive to the surface orientation. (Elliot Hawks, 2011)

FIGURE 4
A limit curve of the Shear vs. Normal pressure of the synthetic adhesive material, when it is sheared in its preferred direction. Each color/shape is an adhesive material with a different hierarchy version. The Hier III (diamond shape) was used for this project. (Aaron Farness, 2010)
To use the design for omnidirectional gripping, three main changes were implemented: the back plate was incorporated into the body of the gripper, the adhesive tile was loaded directly, and the attachment point on the tile was moved above the geometric center of the adhesive (Figure 7, Top).

Because the tile was not loaded by the back plate, the back plate did not need to be a separate component. The tile moves by shearing the compliant support between itself and the body. Since the needed displacement is so low, the spring force created by the sheared support is not large enough to cause a concerning reaction force on the adhesive. The adhesive tile is loaded directly through the tendon, because it was discovered through testing that the ankle does not allow the back plate to lie parallel to an adhered surface. If the gripper’s multiple ankles were allowed to reach negative angles with the adhering surface, they could interfere with the contact between the surface and the adhesive (Figure 7, Middle).

The final change, altering the attachment location between the tendon and the tile, was necessary due to the implementation of a suspension layer. The suspension layer allows the adhesive to have intimate contact with surfaces that are rougher than glass, and to conform to curved surfaces. However, by using the suspension layer with the ankle, a moment is placed on the adhesive tile that tends to peel it off. By attaching the loading string to the top edge of the tile, the moment that is caused by the suspension layer is canceled by the moment produced by the string, which increases the adhesive performance of the mechanism (Figure 7, Bottom).
"These preliminary results suggest that a useful omnidirectional gripping mechanism is feasible to build with the current understanding of the synthetic adhesive and compliant structure."

**TESTING THE DESIGN**

To measure the adhesive strength of the omnidirectional gripper variations, the mechanisms were placed upside down with their opposing tile pairs were loaded sequentially. This ensured that all the pads were sheared against the surface without slipping (Figure 8).

After all of the pads were loaded, the flat plate was pulled up perpendicularly with a force gauge until it detached from the gripper. The resulting adhesive pressure was then calculated by subtracting the weight of the plate and dividing the result by the surface area of the pads. This process was repeated for 1 meter and 3 meter diameter curved sections as well.

**FIGURE 8**
A flat plate test of the first gripper model. The masses at the bottom were used to load each pair of adhesive pads.
RESULTS

Preliminary tests of the omnidirectional grippers yielded the following results, as shown in Figure 9.

<table>
<thead>
<tr>
<th>Flat Plate (Inward Pull)</th>
<th>Set 1 Load (Newton)</th>
<th>Set 2 Load (Newton)</th>
<th>Set 3 Load (Newton)</th>
<th>Adhesive Force (Newton)</th>
<th>Adhesive Pressure (kPa)</th>
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<th>Set 1 Load (Newton)</th>
<th>Set 2 Load (Newton)</th>
<th>Set 3 Load (Newton)</th>
<th>Adhesive Force (Newton)</th>
<th>Adhesive Pressure (kPa)</th>
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<tr>
<td>Test1_Orientation 1</td>
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<td>11.27</td>
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<td>9.31</td>
<td>5.635</td>
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<tr>
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<td>0.63</td>
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<th>Set 1 Load (Newton)</th>
<th>Set 2 Load (Newton)</th>
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</table>

**Figure 9**
Results of preliminary testing. The flat plate was made of glass, and both curved surfaces were fabricated with acrylic. The central four images show the adhesive pad orientations for each corresponding category, and the bottom two images show the difference between inward and outward loading of the mechanism.
GRASPING THE DATA

This is the first time that the synthetic adhesive was used with a mechanism to adhere to a curved surface. The data indicate that the adhesive pressures for the pads are the greatest when adhering to the flat plate, and decrease as the radius of curvature of the adhering surface decreases. This trend is to be expected, as the contact area between each adhesive tile and the surface decreases with the radius of curvature (Figure 10, Top).

Additionally, since the tiles are loaded in shear as antagonistic pairs, the most effective pairing of pads requires that the real area of contact of each pad be maximized. As the two tiles in a set move farther apart, the curvature of the surface begins to reduce the contact area of the pads. Therefore, to maximize the adhesive strength, the distance between pads should be minimized to allow the adhering surface to better approximate a flat plate (Figure 10, Middle).

Finally, the results show that the inwardly loaded gripper arrangement has a higher adhesive pressure than the outwardly loaded arrangement. This is explained by the fact that an inward grasp loads the pads in oppositional shear, resulting in a force that pulls the surface into the mechanism, whereas an outward grasp imposes a resultant force that pushes the surface away and decreases the amount of force that can be supported (Figure 10, Bottom). However, this concern is only applicable when adhering to concave surfaces; the opposite process occurs when adhering to convex surfaces. The outward loading arrangement also offers the benefit of being able to lift flexible materials, since these materials can support tension but not compression (Figure 11).

A gripping mechanism will be deemed practical when it is able to support 80% of the maximum experimental adhesive pressure on a 3 meter diameter section of tubing. The current design of the gripper’s body and ankles allows the mechanism to adhere to both flat and curved objects, independent of their orientation. The maximum adhesive pressure supported on a 3 meter diameter curved surface is 24% of the maximum experimental pressure. These preliminary results suggest that a useful omnidirectional gripping mechanism is feasible to build with the current understanding of the synthetic adhesive and compliant structure.
FIGURE 12
The new proposed arrangement for the adhesive tiles of the gripper (left). Compared to the current arrangement (right), the new arrangement would allow the pads to be closer to one another. This will increase the contact area of each pad, resulting in greater maximum adhesive pressure.

FUTURE WORK

This work shows that adhering to curved surfaces using the synthetic gecko skin is feasible. This greatly extends the range of materials and geometries that can be grasped by the Robotic Vehicles and Manipulators Group at NASA’s Jet Propulsion Lab. Future work will strive to develop a gripper that can support 80% of the maximum adhesive pressure of the material for both curved and flexible surfaces. The first step in achieving this goal will be to manufacture a new design which reduces the distance between the each pad in an antagonistic pair (Figure 12).

Future work will also include finding the optimal distance above the center of pressure of the tile to attach the loading string. By optimizing this distance, the moment on each pad can be minimized, allowing the pads to support a greater external load. After the mechanical design and iteration of the gripper is complete, the final version will be integrated with sensors and constructed using space-rated materials.

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FURTHER READING


The development of functional methods to facilitate carbon fixation through the reduction of \( \text{CO}_2 \) would enable the efficient conversion of solar energy to accessible potential energy in the form of chemical fuels.

Screening Metal Sulfides as Photocatalysts for the Reduction of Carbon Dioxide

**OVERVIEW: the old Earth and the \( \text{CO}_2 \)**

Semiconducting minerals can be used as catalysts in the photoreduction of carbon dioxide to reduced carbon species, such as formic acid, methanol, and methane. Due to the high potentials associated with these reactions and the relative inertness of carbon dioxide as a reactant, the selection of an appropriate semiconducting material proves challenging. Various naturally occurring minerals, most notably sulfide compounds, have attributes favorable for photocatalytic purposes. [1] The development of accessible methods to facilitate carbon fixation through the reduction of \( \text{CO}_2 \) would enable the efficient conversion of solar energy to potential energy in the form of chemical fuels. In addition to its practical application in energy technology, the study of metal–sulfides as catalysts for carbon fixation is relevant to the origins of photosynthesis on prebiotic Earth, as both carbon dioxide and sulfide compounds are thought to have been prevalent early in the Earth’s history.

**MOTIVATION & BACKGROUND**

_Eternal Sunshine for the Renewable Mind_

The increasing global demand for energy necessitates the discovery of a reliable source of renewable energy. Unlike other natural resources, the energy available from sunlight is both decentralized and inexhaustible; more energy in the form of solar radiation strikes the Earth in one hour than the global population consumes in a full year. Eliminating the daily and seasonal variability in solar energy flux by storing this energy in chemical bonds is possibly the most efficient method for fully realizing the potential of the Sun as a reliable source of energy to power the planet. Thus, the efficient and economical conversion of solar power is a key goal in this area of research.
A Natural Solution: Photoreduction

The abundance of atmospheric carbon dioxide, a greenhouse gas that contributes to global warming, due to anthropogenic activities such as the combustion of fossil fuels, makes CO2 an inexpensive and attractive resource for conversion to consumable liquid fuels. However, the reduction of carbon dioxide, a C(+IV) species, into molecules such as methane, is far from simple because CO2 is both kinetically and thermodynamically stable. To overcome this inertness, these reactions require either: (i) the participation of a particularly reactive material, such as a reducing agent of high potential, or (ii) a strong source of energy, such as high temperature or light. We propose using high-energy photons to excite electrons in photocatalysts to potentials sufficient to facilitate the CO2 reduction reaction.

Goldilocks Principle: Semiconductor Selection

Light-driven reactions will require a semiconductor with a large band gap and sufficiently reducing conduction band edge. This ensures that when electrons are excited (via irradiation) to the conduction band from the valence band, they carry enough energy to electrochemically reduce CO2.

Investigations of the absolute energy positions of the conduction and valence bands of common semiconducting materials indicate that the band edges of a handful of transition metal–sulfide compounds may be ideally situated to facilitate this electrochemical reaction.[1] Multiple metal–sulfide catalysts, most notably MnS and ZnS, have been reported to be active photocatalysts for the reduction of carbon dioxide. In addition, the study of metal–sulfide compounds as photoreductants for CO2 is particularly applicable to the investigation of the origins of carbon fixation on early Earth, as many sulfur compounds of transition metals have been isolated as naturally-occurring minerals and are believed to have been prevalent during the planet’s infancy.
“Scans of the photoreductive potential of these mixed metal–sulfide compounds indicate that the addition of ZnS significantly bolsters the catalytic activity of MnS, increasing the observed photocurrent to approximately 2.2 μA for heated samples.”

EXPERIMENTAL DESIGN

The metal–sulfide screening protocol that we have developed is inspired by an analogous combinatorial screening technique implemented in the Solar Materials Discovery program, with some slight modifications.

[2] Primarily, the sensitivity of sulfide compounds to decomposition due to oxidation requires that the synthesis, deposition, and scanning of these compounds be executed within a deoxygenated environment such as a glovebox. As a means of scanning metal–sulfide compounds for activity as photocatalysts, we constructed an electrochemical cell that is operated and monitored using a potentiostat (Figure 2). Synthetic metal–sulfide samples are scanned for activity using the potentiostat’s chronoamperometry feature, which applies a constant voltage and monitors changes in current drawn with respect to time. This system has allowed us to reproducibly observe spikes in current that coincide with the irradiation of deposited sulfide samples. Using this setup, spikes in current observed during irradiation of the sulfide samples are assumed to scale with each material’s effectiveness at reducing CO2.

Results and Discussion

Synthesis and Screening of Manganese Sulfide

We have developed an easily reproducible procedure for the synthesis of nanoparticulate MnS by adapting a protocol reported by Michel et al. [3] The metastable beta and gamma MnS polymorphs, which are pink in color, are synthesized by adding an aqueous solution of MnCl2 to a solution of Na2S and isolating the precipitate. The MnS can be deposited on FTO electrodes by pipetting and evaporating approximately 20 μL of the precipitate suspension. Samples synthesized by this procedure have demonstrated consistent photoactivity, as indicated by spikes in current across the electrochemical system during sample illumination. These peaks, which have magnitudes ranging from approximately 0.5 μA to 1.5 μA, suggest the occurrence of chemical reduction possibly involving the C(IV) species present as carbonate or carbon dioxide (Figure 3). In comparison, iron oxide, a working standard for these experiments, induces spikes in current of approximately 0.68 μA when illuminated in 0.1 M NaOH in our modified electrochemical cell. In light of these similar results, we have adopted manganese sulfide as a comparative standard in our photoreduction experiments.

Additionally, we have found that briefly aging the MnS nanoparticles at an elevated temperature of approximately 200°C can promote the formation of the highly crystalline alpha-MnS polymorph, which we had anticipated to display higher catalytic activity than the beta and gamma phases. This crystalline reorganization was signaled by a significant color change from the light pink color of the mixed beta and gamma phases to the olive-green that is characteristic of the alpha-MnS polymorph. However, screening of alpha-MnS indicates that, contrary to our hypothesis, the alpha crystal structure does not display higher photocatalytic activity than the other polymorphs of MnS.

What Light Through Yonder Laser Breaks?

We have tested two visible light sources for use in our photocatalytic screening experiments, two of which emit light in the visible spectrum. In our system, photons from a violet laser (405 nm) deliver sufficient energy to promote electrons within our sulfide semiconductors from the valence band to the conduction band. Within the conduction band, these electrons have sufficient potential to reduce an equivalent of carbon dioxide, which should result in a measurable increase in the current traveling through the working electrode. When the same semiconductor samples are illuminated with a lower energy green (532 nm) laser, no coincident spikes in current are observed, suggesting that the 532 nm photons impart insufficient energy to excite electrons across the band gap of the sulfide semiconductors. To control for the possibility of misattributing the current spikes detected during irradiation to reactions that do not involve the metal–sulfide as a catalyst, we illuminated bare FTO-coated glass, which is used as a deposition surface for our sulfide catalysts, with the purple (405
nm) laser. Due to the absence of photo-induced current spikes during this experiment, we have continued to use the violet laser for irradiation of the samples.

**Ultraviolet Light as an Alternate Source**

Additionally, we have experimented with replacing the 405 nm laser with a higher energy ultraviolet LED (365 nm) as a means of increasing the number of electrons that carry sufficient energy to reduce CO2. In accord with this hypothesis, we have observed the UV LED to consistently induce higher photocurrent responses from MnS catalysts when compared to illumination events using the purple laser. However, control experiments indicate that conductive, FTO-coated glass produces a spike in current upon irradiation with UV light that is essentially indistinguishable from the photocurrent activity produced by the catalysts themselves. That is, bare FTO (with no MnS) gives spikes in the chronoamperometry plot of current vs. time (Figure 5). As a means of eliminating this confounding variable, we began experimenting with alternate substrates for deposition, such as tin and aluminum foils. However, in preliminary tests of these foil substrates, we observed dramatic oscillation in the dark current measured across the electrochemical system. This instability prevented us from testing the photocatalytic performance of metal sulfides when deposited on these alternative substrates.

**Varying Electrolytes: A Closer Look at Reduction**

As a means of deciphering the nature of the reductive processes occurring during the illumination of our metal–sulfide catalysts, we conducted a series of control experiments in which we systematically adjusted the composition of the electrolyte solution. Using the 405 nm laser, we began by irradiating samples of MnS within a sulfide solution, producing photocurrent peaks of approximately 0.75 µA. The detection of photocurrent peaks during this experiment—despite the lack of carbon species in the electrolyte—suggests the occurrence of alternative reduction reactions, most likely the reduction of protons or water. However, upon the introduction of carbon in the form of NaHCO3 to the electrolyte, the magnitude of the observed photocurrent peaks more than doubled, as the average peak size increased to approximately 1.6 to 2.0 µA. This significant increase in current suggests the emergence of a new reaction, possibly due to the reduction of carbon (IV) species.

**Nothing Manganese Can Stay**

Complexes of various transition metals, including zinc and copper, have been observed to display activity as catalysts in reduction reactions upon irradiation. While evidence of photocatalytic activity in pure metal sulfides has been reported, the potential of mixed-metal sulfides as catalysts has remained relatively unexplored. Thus far, our combinatorial search for highly active mixed-metal reduction catalysts has included eight metal–sulfide dopants: cerium, copper, iron(II), iron(III), magnesium, nickel, tin, and zinc. Of these metals, we have observed copper, iron(II), and zinc to increase the measured photoactivity of manganese sulfide. Motivated by reports of ZnS-facilitated photoreduction,[4] we began to examine the possibility of introducing ZnS as a dopant within our MnS system. Scans of the photo-reductive potential of these mixed metal–sulfide compounds indicate that the addition of ZnS significantly bolsters the catalytic activity of MnS, increasing the observed photocurrent to approximately 2.2 µA for heated samples.

Similarly, the addition of small amounts of copper(II) and iron(III) to a manganese sulfide solution dramatically increased the observed photocatalytic activity of MnS. However, both copper and iron appeared to inhibit the adhesion of the metal sulfide sample to the FTO-glass substrate. In each case, heating the spotted sample at approximately 90°C helped to create a smooth, cohesive, and ultimately photo-reactive sulfide film.

**CONCLUSION**

The abundance and low cost of CO2 and other carbon(IV) species make them attractive feedstocks for the production of solar fuels, but the reduction of carbon dioxide is hindered by the molecule’s thermodynamic and kinetic stability. Our results suggest that a number of metal–sulfide compounds—most notably manganese sulfide supplemented with copper, iron (II), or zinc—have the potential to catalyze this difficult photoreduction reaction to enable the efficient and economical conversion of solar energy.
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I wish to thank Drs. Harry Gray, Jay Winkler, and Paul Bracher for facilitating my research through thoughtful guidance and enthusiastic support. Additionally, I am greatly appreciative of the CCI Solar and the Caltech SURF programs for funding my research fellowship.

FURTHER READING

FIGURE 3
A chronoamperogram displaying changes in the current drawn across an electrochemical system over time is displayed below. The working electrode is made of FTO-glass spotted with nanoparticulate MnS. A 405 nm violet laser was used to illuminate the sample of MnS in an electrolyte solution of 7.2 mM Na2S and 2.5 mM NaHCO3.

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FURTHER READING
Abstract

The cognitive and neural mechanisms that support language production are not yet fully understood. Based on previous work language-sensitive brain regions respond more strongly to event description conditions than to conditions where participants name three unrelated objects. The mechanism by which subjects respond to event description conditions involves not only accessing the lexico-semantic representations of three content words but also constructing a larger meaning from those component parts. On the other hand naming three unrelated objects activates the “multiple demand” brain regions, which respond to challenging tasks, because describing objects is more cognitively demanding than simply reading words. The goal of the current project is to examine brain activity during naming tasks using functional magnetic resonance imaging (fMRI). The functional region-of-interest analyses will be complemented by more traditional whole-brain analysis methods.
Background

The process of language production begins when the speaker decides to convey a thought into language. The message represents the conceptual or semantic features of a to-be-produced word. Next the speaker selects a given lemma or word that represents the message. Lemmas enable access to the phonological and syntactic properties of a word; a lemma is the conceptual representation of an abstract idea which contains the meaning, but not the sounds, of a word. Then, speakers select the lexemes, which are whole-word representations of the phonology of a lemma, necessary to pronounce words. For example at the lemma level, “doorbell” would specified as a singular noun, and would be presented at the lexeme level as how the word “doorbell” sounds. Segment retrieval occurs next, at which point the brain retrieves individual speech sounds that compose a word. These individual speech sounds are then organized syllable by syllable prior to initiation of the speech-motor stage, in which the original thought is articulated (Ferreira, 2010).

Although linguistic expression has been studied and broken down into representations, the neurological mechanisms behind language production are not yet fully understood. Pierre Paul Broca’s work on aphasic patients in the mid-19th century was the first documented proof of localization of a brain function. Broca identified the region as a portion of the brain frontal lobe linked to the language process. Broca was able to prove the idea that a brain region can be correlated to a given function after performing an autopsy on patient “Tan” who
had suffered from loss of speech and paralysis. Examination of Tan’s brain indicated a brain lesion in the frontal lobe of the left cerebral hemisphere, supporting the hypothesis that the left frontal lobe is specialized in language production. Further neurological studies continued to emerge indicating that certain areas of the brain, such as Broca’s area and specific regions of the temporal lobe, are responsible for articulated language function.

New technological advances, including fMRI and EEG, have allowed researchers to better locate brain regions associated with language production. Unfortunately, imaging studies also have several problems in that brain mapping may become blurred and inaccurate.

New technological advances, including fMRI and EEG, have allowed researchers to better locate brain regions associated with language production. A number of regions are implicated in language production and syntactical language processing, such as the primary motor and somatosensory cortices, auditory cortical areas, and supplementary motor area (SMA) as well as select regions of the parietal cortex (Brodmann Areas 6/7) and the insula (Haller et al., 2005; Kircher et al., 2011; Gernsbacher & Kaschak, 2003; Kaan and Swaab, 2002). Unfortunately, imaging studies also have several problems in terms of the mapping and analysis of brain function. One issue with fMRI is that, due to variances in individual brain size and shape, brain mapping may become blurred and inaccurate. Another hindrance with fMRI studies involves the heterogeneous property of the brain. Heterogeneity refers to patches of cells with different properties. Because distinct patches of cells in the Broca’s area have disparate functions, fMRI analysis of activation patterns in IFG/Broca’s area can be blurred and inaccurate. This is a result of multiple signal locations arising from the domain-general region (multiple demand network) or language-specific region activity within the Broca’s Area. Scientists can now minimize individual brain variation in fMRI studies by specifically selecting regions of the brain activated by the main language task, thus improving image resolution.

Previous work in the Kanwisher Lab using fMRI has shown that there exist highly specialized regions in the brain associated with language processing (Fedorenko et al., 2011). Other areas of the brain have been identified as responsible for cognition at a multifunctional level. Such regions include the domain-general multiple demand network in the fronto-parietal region, which has been implicated in separation and assembly of new task parts, detecting cognitive conflict, and anticipation of a demanding decision. Ultimately we sought the connection between previously indicated brain regions and their role in complex language processing. (Duncan et al., 2010).

The Role of the Multiple Demand Network in Language Processing

The main goal of this project is to identify the role of the multiple demand network and specialized areas of the brain that support language comprehension in overt production via appropriate fMRI techniques. For the multiple demand network-language studies, we use fMRI to study brain activation as participants perform various tasks. The study incorporates a blocked design lasting 4 seconds. We have a collection of single-word images including 96 humans, objects, and animals, as well as a collection of events including 32 human-human, human-object, and
human-animal events. We next ask participants to describe the image or read text while recording their responses. In order to create the experimental script for subsequent experiments, the lab uses VisionEgg, a python-based platform for presenting visual and auditory materials, and the TrioTim 3 Tesla MRI scanner for data collection.

The participant is run on the language localizer, multiple domain (MD)-system localizer, and the articulation localizer. In the multiple demand localizer task participants are asked to describe events and single objects and read sentences and single words during the critical language task. The critical language task involves the use of images, which are described, and words, which are read. Once the participants have responded, it is possible to match their recorded response with brain activity levels during fMRI. Our initial results indicate that the multiple demand network, particularly the pars orbitalis of the left inferior frontal gyrus (LIFGop) (indicated by red circle in Figure 1), responds more robustly to the naming rather than the reading tasks. Naming an object or event is more taxing than reading lists of words or a sentence, causing activation of the multiple demand network, a network that generally responds more robustly to cognitively challenging rather than simplistic tasks.

Figure 1 Key
LIFGop=left inferior frontal gyrus pars opercularis  
RIFGop=right inferior frontal gyrus pars opercularis  
LMFG=left middle frontal gyrus  
RMFG=right middle frontal gyrus  
LMFGorb=left middle frontal gyrus pars orbitalis  
RMFGorb=right middle frontal gyrus pars orbitalis  
LPreCG=left precentral gyrus  
RPreCG=right precentral gyrus  
LIns=left insula  
RIns=right insula  
LSMA=left supplementary motor area  
RSMA=right supplementary motor area  
LParInf=left inferior parietal lobe  
RParInf=right inferior parietal lobe  
LPariSup=left superior parietal lobe  
RPariSup=right superior parietal lobe  
LACC=left anterior cingulate cortex  
RACC=right anterior cingulate cortex

Figure 1
Activation of regions identified as part of the multiple demand region using the multiple demand network localizer task. Data represents average of first two subjects run under blocked design.
The Role of Language Specialized Regions in Language Processing

Alternatively, the language functional regions of interest tended to respond more robustly to events rather than to single objects. Both the left inferior frontal gyrus (LIFG) and left middle frontal gyrus (LMFG) (indicated by red circle in Figure 2) responded with higher activity in the reading sentences and naming events versus reading words and naming objects tasks, respectively. Since the language regions are responsible for higher level linguistic tasks, we might expect that an event that incorporates syntax, higher level meaning, and other sentence complexities, would cause greater response than unconnected single objects.

In the language localizer task, participants read sentences, sequences of words, and sequences of pronounceable non-words. Brain region activation contrasts between sentences and non-words, allowing for identification of brain regions important for complicated linguistic comprehension. The Critical Language Production Task involves both a reading or naming condition and a words list or sentence condition (see Figure 3). Unexpected results included the fact that some objects caused greater response than events in a couple of functional regions of interest of the language specialized areas, namely the left inferior frontal gyrus pars opercularis and left anterior temporal cortex (see Figure 2). Naming conditions caused more robust responses in the language forming regions than reading conditions in the left middle frontal gyrus, left inferior frontal gyrus, and left angular gyrus. Additionally, though most regions in the multiple demand network responded more strongly to naming events/objects than to reading sentences/words as expected, a few regions deviated from this behavior, such as the left inferior parietal lobe (see Figure 1).
“fMRI analysis of activation patterns in IFG/Broca’s area can be blurred and inaccurate. This is a result of multiple signal locations arising from the domain-general region (multiple demand network) or language-specific region activity within the Broca’s Area.”

Further Reading:
“A number of regions are implicated in language production and syntactical language processing, such as the primary motor and somatosensory cortices, auditory cortical areas, and supplementary motor area (SMA), etc.”

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Impact of the Topography on the North American Monsoon
ABSTRACT

From New Mexico to New Delhi, monsoons are some of the most prominent features of the large-scale summertime circulation, but their fundamental mechanisms are not well understood. In this paper, we study the impact of topography on the North American Monsoon. Elevated topography, such as mountain ranges, causes a phenomenon called thermal forcing, or the heating of atmosphere to higher temperatures. Recent studies propose that a second effect, mechanical forcing, is another significant factor. Mountain ranges not only raise air flow to higher elevations, but can also act as topographic barriers that obstruct airflow and effect downstream flow. In this study, we looked at the effects of the Rocky Mountains on the North American Monsoon by comparing precipitation, wind and moisture transport patterns with the topography intact or removed in several General Circulation Models (GCM). Results show that the Rocky Mountains do have a large impact on the circulation of the North American monsoon season, specifically in a South-eastern shift of the monsoon.
Monsoons impact agriculture, climate and economics around the world, but many of the mechanisms responsible for monsoons are poorly understood.
INTRODUCTION

Monsoons are the seasonal reversal in wind and precipitation patterns resulting from an asymmetric heating of the land and sea. Although the most dramatic monsoon develops over Asia, monsoons are among the most prominent features of large scale atmospheric circulation around the world, including North America. Also known as the Mexican monsoon and the Arizona monsoon, the North American monsoon begins in late May and extends through northwestern Mexico into the southwest United States by mid-July, with seasonal reversal of pressure, wind patterns, energy and mass transfers typical of monsoons.

TWENTY THOUSAND FEET ABOVE THE SEA

The interior of the North American Monsoon region is characterized by several large upland areas such as the Colorado and the Mexican Plateaus and the Rocky Mountains. There are also two lowland areas associated with the NA monsoon which play a critical role in the formation of the thermal low.

In this paper, we focus on the role of elevated topography, which affects monsoon circulation and development through both thermal and mechanical forcing. Thermal forcing comes about when the atmosphere over elevated topography is heated to higher temperatures than it is over adjacent non-elevated surfaces, which mechanical forcing states that mountains act as a mechanical obstacle to flow, changing the distribution of wind patterns, regions of ascending and descending motions, and with them, the distribution of precipitation. It was popularly thought that thermal forcing played a much more significant role than mechanical forcing, but the quasi-equilibrium theory, an increasingly popular theory of the effect of moist convection on larger-scale circulations, suggests that convection, rather than the heating itself, controls the vertical temperature profile. By this view, convections quickly restore the atmosphere to convective neutrality, therefore constraining temperatures to follow a moist adiabat and to be coupled with lower-level equivalent potential temperatures, suggesting that mechanical forcing may play a more significant role than previously thought.
The Rocky Mountains significantly impact North American monsoon circulation through mechanisms such as precipitation, wind and moisture transport patterns.

Methods/Results: A MOUNTAINOUS PROPOSAL

In this project, we looked specifically at the Rocky Mountains, a major mountain range extending from Western Canada to New Mexico and compared the data from GCM models run with topography intact with ones run with the topography removed.

SELECTING A MODEL

In order to select a model, we compared various GCMs, including SM2, AM2, CAM3, and CMAP, to the GPCP precipitation data from NASA to select the most accurate model in regards to the North American Monsoon.

CAM3 (Community Atmosphere Model) was the most accurate prediction of actual monsoon precipitation distribution, especially in the south-western and western United States.

For further comparison, we compared the equivalent potential temperatures, a thermodynamic quantity that is a good indicator of moist energy content and the stability of the atmosphere to vertical motions, from the CAM3 model to data from ERA-40 (the 40 year European Centre for Medium-Range Weather Forecasts Re-Analysis). There were slight differences in the two figures, but the general pattern is similar, giving us further confidence that the CAM3 model provides a realistic simulation of the North American Monsoon.
Figure 1. NCL plots of precipitation in North America in July

(a) GPCP precipitation data

(b) SM2.1 precipitation data

(c) CAM3 precipitation data

(d) AM2.1 precipitation data

(e) CMAP precipitation data

Figure 2. Plots of the equivalent potential temperature at near surface pressure (925 hPa) in July

(a) Equivalent potential temperature from CAM3 model

(b) Equivalent potential temperature from ERA-40 data
ROCKY MOUNTAIN PICTURE SHOW

A. Changes In Precipitation

Data was collected using CAM3 with the Rockies removed from the model, from 15°N to 55°N latitude and from 150°E to 120°W longitude. That data was compared to a control run with full topography. In terms of changes in precipitation pattern (Figure 4), without the Rockies, the Great Plains region, the Southwest United States, and Northwest Mexico (around Baja California) all become much drier while precipitation around central Mexico seems to be slightly higher.

Figure 3. Comparison of total precipitation rate in July of CAM3 runs with and without Rocky Mountains.

(a) With Rockies

(b) Without Rockies

In the absence of the Rockies, precipitation is shifted southeast, possibly because winds from the Gulf of Mexico don’t extend as far north while winds from the Pacific anticyclone extend further east.

B. Changes In Wind Pattern

To further analyze this hypothesis, we also looked at changes in wind patterns, which are strongly related to precipitation distribution. The results of the zonal and meridional winds show that, as predicted, wind patterns are altered, especially an eastward extension of the Pacific anticyclone. Winds from the Gulf of Mexico typically come in and flow north up to 40°N latitude, but without the Rockies, winds from the Gulf extend only to about 30°N, then move westward, through northern Mexico, and back down towards the Pacific. We note the cyclonic motion in the Western United States around this latitude, which is noticeably missing when topography is removed.

Figure 4. Comparison of the winds with and without the Rockies.
C. Equivalent Potential Temperature

Next, zonal and meridional winds were overlaid on the equivalent potential temperature.

As Figure 5 shows, the monsoon moves further south in the absence of the Rocky Mountains. The equivalent potential temperature decreases near the western United States and northwestern Mexico, signaling less precipitation (consistent with Figure 4). The wind patterns are also different; there appears to be a strong cyclonic circulation in the western US around the peak of the equivalent potential temperature contour. Without the mountains, this circulation decreases in latitude and intensity to just north of the Gulf of California. This appears to be from the fact that winds from the Gulf of Mexico do not extend as far north as in the model with full topography.

D. Meridional Winds

Due to the different wind patterns that appeared in Figure 5, we took a more detailed look at the meridional winds from 95°W to 115°W, averaged at all latitudes, for the month of July. The winds were taken close to surface pressure. As shown in Figure 7, between the latitudes of 30°N and 60°N the meridional winds in the model with full topography were stronger than those in the model with the topography removed. Furthermore, the maximum of the meridional (North South) winds for the model without topography is around 33°N, compared to about 40°N for the model with topography. Comparing this with Figure 5 we see that the results are consistent.
Monsoonal circulations affect the climate of nearly a quarter of the globe and bring with them a “rainy season” that helps to sustain half the world’s population but much of the mechanisms that drive monsoons are not well understood. In North America, in particular, our results demonstrate that the Rocky Mountains do have a large impact on the circulation of the North American monsoon season, specifically in a Southeastern shift of the monsoon. Our data shows that the Rocky Mountains can alter precipitation patterns not only by redirecting wind patterns from the Pacific and the Gulf of Mexico, but also by altering the higher and lower level equivalent potential temperature distribution. Although more work needs to be done to clarify the roles of thermal and mechanical forcing in monsoon patterning, it is clear that elevated topography such as the Rocky Mountains do significantly affect monsoon precipitation distribution. Significant topographic changes have resulted from recently human geomorphic activities, and it is only by further analyzing the role of topography can we accurately predict future monsoon patterns.

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REFERENCES


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